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# Gas Absorption by Methyl oleate and Its Stereo-isomer

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(Text-figs. 1–15; Tables 1–3)

## INTRODUCTION

It was reported in the preceding publications[1), 2), 3)], that oily substances like glycerides, sperm waxes, etc. absorb much more amount of gases (oxygen, nitrogen and carbon dioxide) than water does. However, these oily matters differed considerably one from another, in the capacity of absorbing a gas (solubility) and especially in the rate of gas absorption. From these results, it became almost clear that the esters of higher fatty acids with higher monovalent alcohols which constitute the natural components of sperm wax, show conspicuously higher absorbing capacity and especially higher absorption rate than ordinary glycerides.

Apart from a possible role that such substances might play in the physiology of the sperm whale, a question arose to the author: what causes the capacity and the rate of gas absorption to differ so much among oily substances. At the outset, it occurred to the author that these properties might be related to the length, or at least, to the shape of molecules which constitute these oily substances. One way to verify this hypothetical idea, seems to make comparison between a pair of substances which are *cis-trans* isomers to each other.

The present article is concerned chiefly with a research on the absorption of carbon dioxide, nitrogen, and oxygen by methyl oleate and its *trans*-isomer, methyl elaidate. In addition, absorption of these gases by free oleic acid and water was also investigated for comparison.

## ANALYTICAL TREATMENT ADOPTED

Some treatment was introduced in order to determine the experimental formula expressing the relation between the absorbed amount of a gas and the time elapsed. Therefore, a brief comment will be made here to clarify the introduction.

As announced in the previous reports[2), 3)], for a constant temperature-absorption test of a gas, which is relatively little soluble in a solvent, the relation between the absorbed amount which is experimentally measured, and the time can be approximately stated by a formula, reading

$$y = A(1 - e^{-\alpha t}), \quad \cdots\cdots(1)$$

where $y$ is the absorbed quantity of a gas until a time $t$, $A$, the maximum quantity

of the same gas absorbed at the saturated state (solubility), and $\alpha$, a constant characteristic of a combination of a gas and a solvent.

Thus, with oxygen and nitrogen, Formula (1) is valid in fairly well approximation. However, for such a gas as carbon dioxide, which is much more soluble than oxygen or nitrogen in various solvents, the results of the absorption tests were not adequately expressed by Formula (1).

On the other hand, in the present work as well as in the preceding works, each absorption test consists in enclosing a definite quantity of a gas and a solvent in a pressure-bottle of a definite volume, and recording punctually, the decrease in pressure caused by absorption, by means of a manometer. In other words, our absorption tests are so constructed that the pressure is not kept constant, but decreasing with the process. Consequently $A$ cannot be strictly a constant, throughout a whole course of an absorption test, but is really a variable dependent upon the time or more directly upon the pressure changing with the progress of time. It can be treated as a practically constant, only when the change in pressure during a course is sufficiently small.

In a brief analytical consideration, if the plot of log $(A-y)$ depicts a decreasing straight line against $t$, as abscissae, Formula (1) is sure to hold for this relation, and *vice versa*. That is, these two events are mathematically equivalent. Therefore, it is a corollary that if log $(A-y)$ does not follow such a straight line against $t$, Formula (1) can never be valid for our relation. Now, in the present cases, if a curve obtained becomes other than a straight line, it is ascribable to either that Formula (1) cannot be valid essentially for this relation or that the curve does not become a straight line, because of our erroneous treatment of data. Inferred from mentioned in the last paragraph, the most possible among the erroneous treatments, is that we are dealing with $A$, as a constant, in spite of its variability with the time.

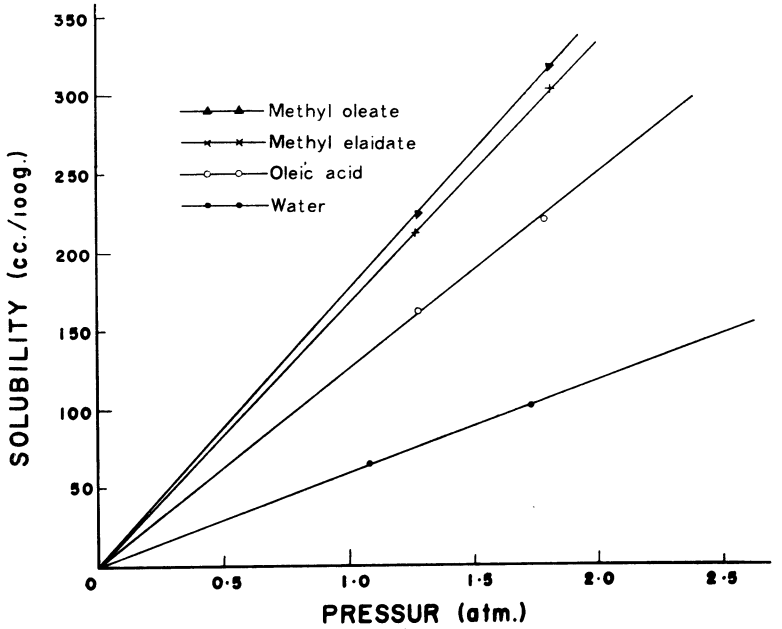
Really, in our experiments, it is very certain that the smaller the change in pressure during an absorption test, the validity of Formula (1) becomes more and more complete. Herefrom a prospect emerges that Formula (1) would be exactly valid, if the pressure might be kept constant, whereby $A$ constitutes a real constant. Then, in our cases, the problem goes whether the data obtained by the experiment with decreasing pressures, can be converted into the data which would be obtained in a constant pressure experiment.

The functional relationship between the solubility of a gas and the pressure is known as Henry-Raoult's law,

$$A = k\,p, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

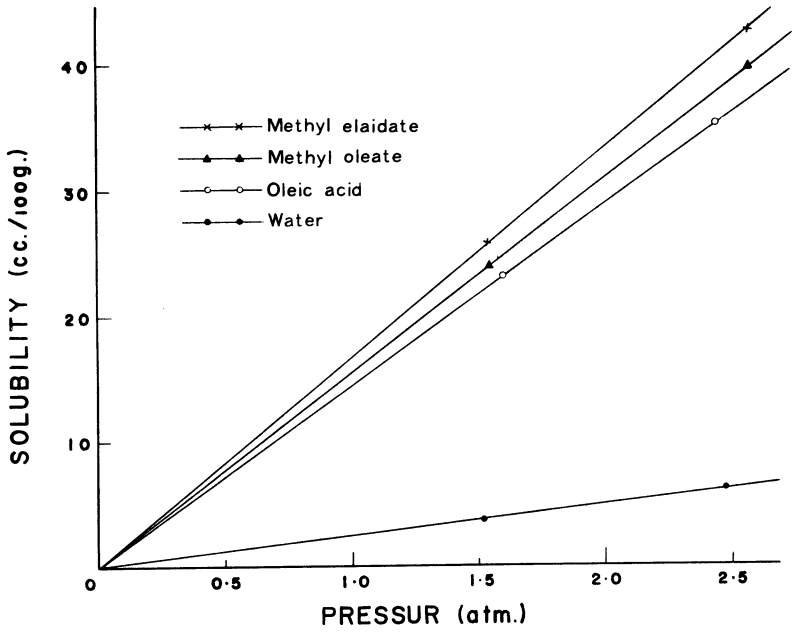
where $A$ denotes the solubility of a gas, $p$, the pressure applied and $k$, a constant definite for a combination of a gas and a solvent, and for a given temperature. Then, in our case, if we denote the solubility of a gas at the initial pressure, $p_i$, by $A_i$, and the solubility at any pressure, $p$, by $A$, we have,

$$A = \frac{p}{p_i} A_i. \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$




Text-fig. 1. Solubility (cc/100 g) of carbon dioxide in various materials, plotted against pressure (atm. pres.)

In the case of water, the pressure is total pressure observed minus 42.2 mm Hg, the vapor pressure of water at 35°C.




Text-fig. 2. Solubility (cc/100g) of oxygen in various materials, plotted against pressure (atm. pres.)

In the case of water, the pressure is total pressure observed minus 42.2 mm Hg, the vapor pressure of water at 35°C.

For combining Formula (1) and (3), we obtain

$$\frac{p_i}{p} y = A_i(1 - e^{-\alpha t}). \quad \cdots\cdots(4)$$

Formula (4) represents the relationship between the absorbed quantity of a gas (left side term) in a constant pressure absorption test in which the pressure is $p_i$, and the time, $t$. This term may be adequately designated by $z$, or other symbols. $A_i$ can be estimated from the maximum value of $\frac{p_i}{p} y$.

In the present work, this revision was performed upon any absorbed amount obtained, not only with carbon dioxide but also in the cases of oxygen and nitrogen, with the result of $\log\left(A_i - \frac{p_i}{p} y\right)$ becoming a straight line against $t$, within the limits of experimental error. It becomes clear that our relation can be essentially stated by Formula (4).

## EXPERIMENTAL

### Materials

Physical and chemical properties of the materials used are given in Table 1. They were prepared as follows.

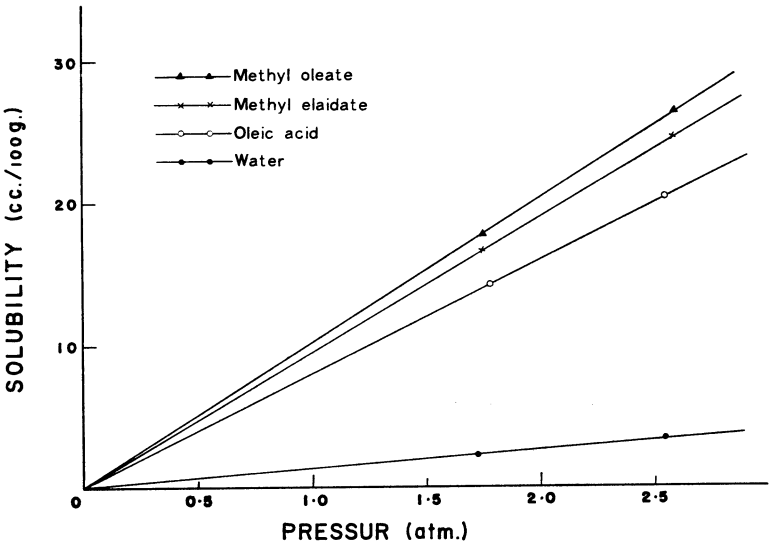
Table 1 Physical and chemical properties of materials

| Material | $d_4^{20}$ | $\eta_{20}$ c.p. | Bp. | I. V. | S. V. |
|---|---|---|---|---|---|
| Methyl oleate | 0.869 | 6.02 | 205–8 (12.5 mm.) | 84.8 | 193.4 |
| Methyl elaidate | 0.863 | 6.86 | 195–9 (10 mm.) | 85.5 | 193.7 |
| Oleic acid | 0.885 | 31.90 | —— | 89.5 | —— |
| Water | 0.994 | 1.00 | —— | —— | —— |

*Methyl oleate.*—Commercial oleic acid as a starting material, was first subjected to "wintering" with 2 times its volume of acetone, to remove solid fatty acids. Then, the remaining solid acids were removed by Twitchel's method and higher unsaturated acids, by Li-salt-alcohol method. This was followed by methylation, and methylated products were subjected to fractional distillation *in vacuo*.

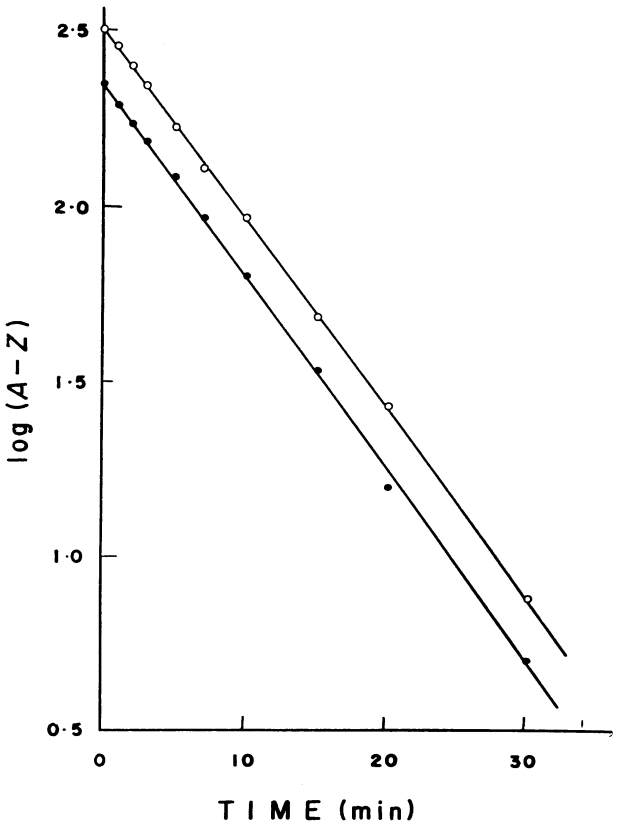
*Oleic acid.*—Obtained by liberation of the methyl oleate purified by the method described above.

*Methyl elaidate.*—Some of the oleic acid thus refined, was elaidinized by treating with Poutet's reagent[4], which was prepared from 6 g of Hg and 15.6 cc of nitric acid having density of 1.42. One part of Poutet's reagent was added to 12 parts of oleic acid. After over-night standing at 15–18°C, the mixture was found solidified as a whole. Elaidic acid was isolated from the mixture, by means of Pb-salt-alcohol method, and purified by taking advantage of the difference in solubility of lead elaidate and lead oleate in petroleum ether having Bp. of 40–60°C.




Text-fig. 3. Solubility (cc/100 g) of nitrogen in various materials, plotted against pressure (atm. pres.)

In the case of water, the pressure is total pressure observed minus 42.2 mm Hg, the vapor pressure of water at 35°C.




Text-fig. 4. Log $(A-z)$ - $t$ diagram for carbon dioxide-methyl oleate.

Since Poutet, a variety of methods of isomerization of oleic acid has been presented by many authors[5),6),7)]. However, Poutet's method appears one of the most recommended one, because of the higher yield of elaidic acid, because of the comparatively small proportion of addition products, and further because of the simplicity of the procedure. In the present cases, the yield of elaidic acid always exceeded 60% of oleic acid as a starting material, and the proportion of addition products seems to be as small as indicated by its iodine value (Table 1). Melting point of the free elaidic acid obtained is 42.2°C, and its solidifying point is 38°C.

The free elaidic acid was methylated, and the methylated products were subjected to fractional distillation *in vacuo*.

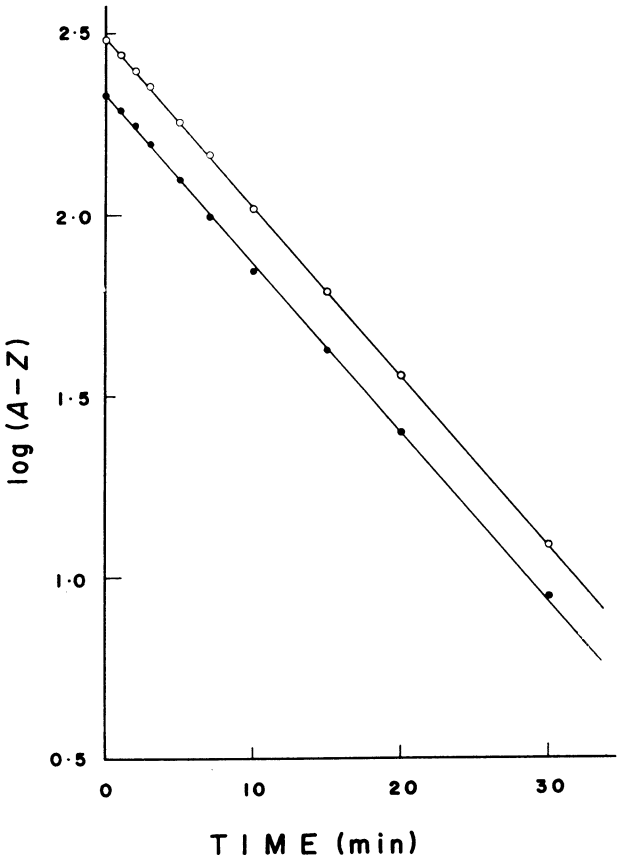
*Water*.—Distilled twice and de-ionized by means of ion-exchange resin.

**Apparatus and Procedure**

Apparatus and procedure employed were the same as had been detailed in the previous report[1)]. Therefore, only a brief description needs to be given. Throughout the present series of experiments, every absorption test was carried out with 100 g of material, at the temperature controlled at $35 \pm 0.05$°C. Deaeration preceding each absorption test was performed in almost the same way as described in the earlier paper[1)]. After enclosing the liquid material in a pressure-bottle, the major part of deaeration took place in a boiling water bath, in vacuum below 1 mm Hg, during a period more than twice as long as it took in the subsequent absorption test. Following this, the material in the pressure-bottle was allowed to stand at the same reduced pressure for an hour, in a large thermostat maintained at $35 \pm 0.05°$, for the purpose of permitting the thermal equilibrium between the inside and the outside of the bottle. Then, closing a sucking stop-cock, a gas was introduced into the bottle from a gas-reservoir which had been maintained also at $35 \pm 0.05°$, until a desired reading of a mercury manometer was reached, and the measurement was started.

In the case of water, however, the foregoing deaeration cannot be applied, because the vapor pressure of water is so high. Water was thoroughly boiled and cooled under reduced pressure. From this, 101 cc was pipetted into the pressure-bottle, care being taken not to be bubbled or disturbed. After enclosing the bottle, it was suctioned up to about 40 mm Hg (the vapor pressure of water at 35° being 42.2 mm), in the said thermostat. When this pressure was reached, sucking stop-cock was closed, and the bottle was allowed to stand for an hour in this state. Finally, the bottle was evacuated at an utmost rate for exactly 1 min., and the next procedure was started. At the end of the absorption test, the water remained in the bottle was thoroughly and carefully weighed; it was always found 99.5–100 g of water still remained in the bottle.

Mechanical arrangements to effect constant movement of the pressure-bottle and other experimental conditions were almost alike to those which had been employed in the previous works[1),2),3)].




Text-fig. 5. Log $(A-z)$ - $t$ diagram for carbon dioxide-methyl elaidate.

## DETERMINATION OF ABSORBED VOLUME OF A GAS

In the present work, as noted above (p. 108), the decrease in pressure caused by absorption was measured at constant volume. So that, we cannot find directly from experiments, the decrease in volume, and therefore, the absorbed volume of a gas. This decrease in volume or the absorbed volume of a gas by a solvent (the identity of the two quantities will be discussed later, p. 114), was calculated from the decrease in pressure, in the following manner.

Suppose that the pressure be kept at the initial constant value, throughout the whole process of an absorption test. Then, the volume of the gas must decrease at this constant pressure, instead of occurring of the decrease in pressure at the constant volume.

If we write $p_i$ and $(p_i - \Delta p)$, for the pressure at the beginning and at any time, $t$, respectively, and $v$, for the volume of the gas, then, from the perfect gas law, we have

$$(p_i - \Delta p)v = p_i(v - \Delta v), \quad \cdots\cdots(5)$$

where $\Delta v$ represents the decrease in volume which would occur until a time, $t$, if the pressure were kept at the constant value, $p_i$. From Equation (5), we obtain

$$\Delta v = \frac{v}{p_i} \Delta p. \quad \cdots\cdots(6)$$

Furthermore, we can write, in terms of the standard state,

$$\Delta v_0 = \frac{T_0}{T} \frac{1}{p_0} v \, \Delta p, \quad \cdots\cdots(7)$$

where $\Delta v_0$ denotes the decrease in volume of the gas reduced to standard state, $T_0 = 273^\circ$K, $T = 308^\circ$K (in the present case), $p_0 = 760$ mm Hg, and $v$, the whole internal space of the closed system, which was estimated at $684 \pm 0.5$ cc, including the inner space of rubber and glass tubings, minus the volume of a material taken into the bottle.

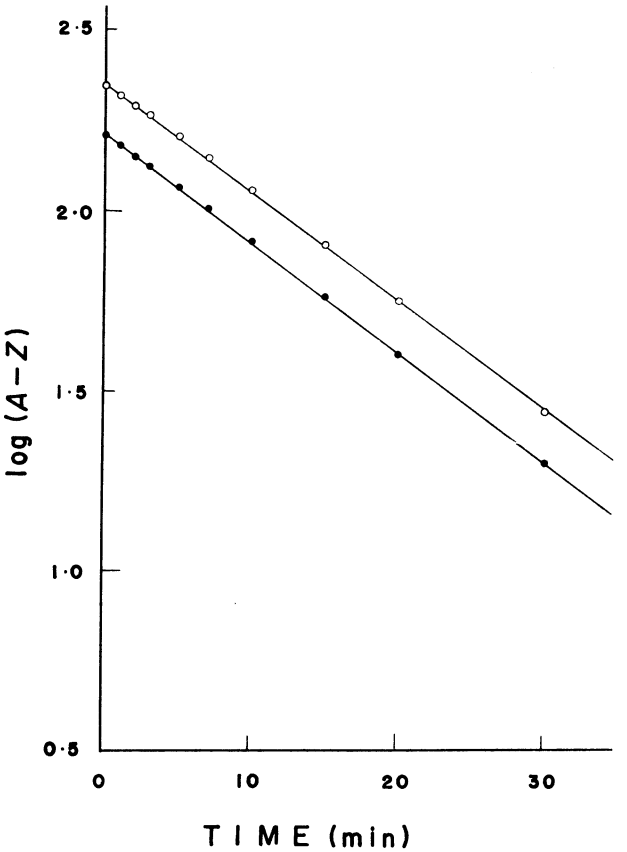
Thus, the decrease in pressure observed, multiplied by the constant factor $\frac{T_0}{T} \frac{1}{p_0} v$, gives the decrease in volume of the gas as reduced to standard state. This decrease in volume must represent the volume of the gas that has been absorbed in the solvent, provided that there exists no other source of absorption nor the leakage of the gas, out of the closed system. Whether these conditions are satisfied or not, could be checked by a blind test.

Surely, we must take several sources of error into account. In the first place, if the volume expansion of the liquid phase occurs by $\Delta D$, upon absorption of a gas, the real decrease in volume must be, according to Equation (7),

$$\Delta v_0 = \frac{T_0}{T} \frac{1}{p_0} (v - \Delta D) \Delta p, \quad \cdots\cdots(8)$$

and this amount of the gas must be transferred to the liquid. Therefore, the real absorbed amount is to be smaller than the amount calculated by Equation (7). However, the volume expansion of a liquid by absorption of a gas is usually so small as to be ignored in our present calculations. For most gas-liquid systems (solutions), the volume expansion of solution does not exceed 0.25% of the standard volume of the gas absorbed[8]. Thus, when a gas is dissolved by 100 cc at standard state, $\Delta D$ can be only 0.25 cc, at the highest estimate; this volume is able to be neglected, as compared with the magnitude of $v$.

The second source of error which may be of more importance and therefore must be subjected to more serious examination, will be the one which must originate from applying the perfect gas law without any correction, in the calculation of the decrease in volume. In this connection, examination was made on the difference that would emerge in the value of $\Delta v$, in Equation (6), when we apply an equation of state of imperfect gas, instead of the perfect gas equation. We chose for this purpose, as an equation of state[9],



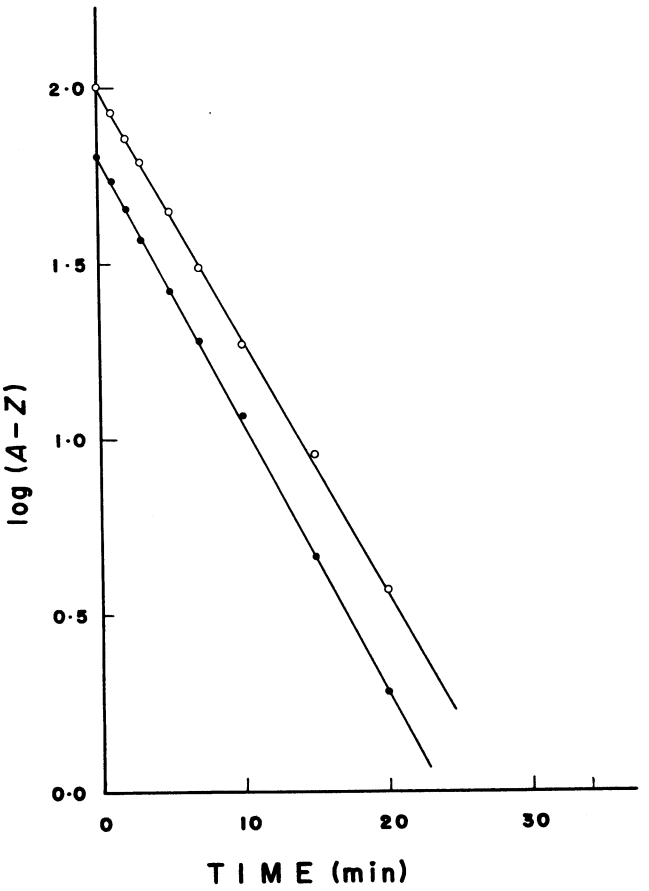

Text-fig. 6. Log $(A-z)$ - $t$ diagram for carbon dioxide-oleic acid.

$$\frac{PV}{nRT} = 1 + \left(b - \frac{a}{RT}\right)\left(\frac{n}{V}\right). \quad \text{.....(9)}$$

The result of the calculations showed that $\Delta v$ calculated from Equation (9) is by 1% greater than that calculated from perfect gas equation, in the case of carbon dioxide, assuming the initial pressure, $p_i$, as 3 atm. pressures, and the decrease in pressure, $\Delta p$, as 0.5 atm. pressure. In the present work, there was involved no instance in which $p_i$ and $\Delta p$ exceed these limits. So that, an error of 1% can be regarded as the highest estimate. Furthermore, because carbon dioxide is the most distant from the perfect gas, among the gases employed, the error in $\Delta v$ must be far smaller in the case of oxygen or nitrogen.

## ANALYSIS OF DATA

As detailed in a forgoing chapter (p. 107), the relation between the absorbed volume of a gas and the time, is stated by Formula (4), in which replacing $\frac{p_i}{p} y$




Text-fig. 7. Log $(A-z)$ - $t$ diagram for carbon dioxide-water

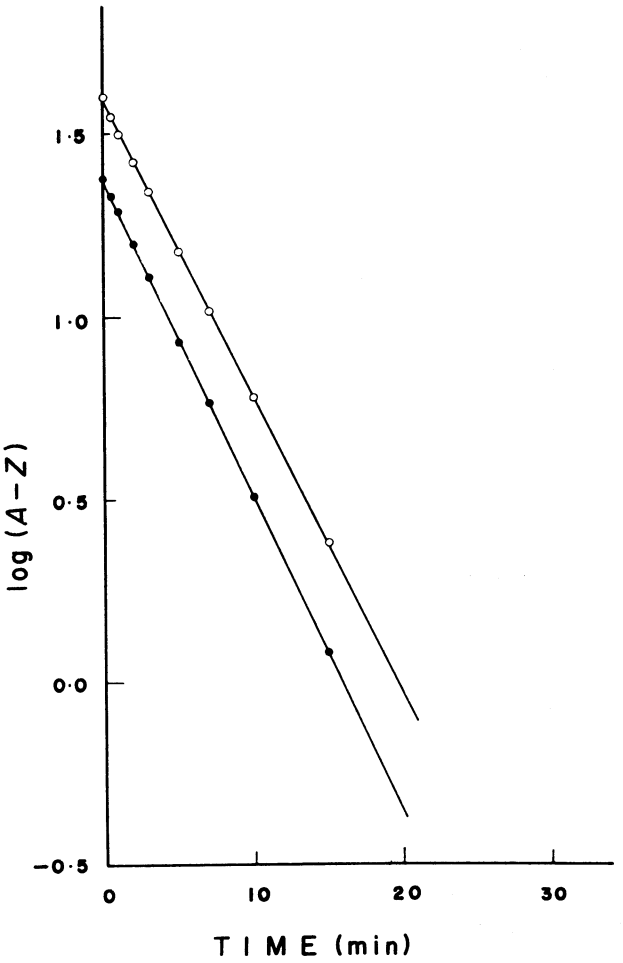
with $z$, and $A_i$ with $A$, we have

$$z = A(1 - e^{-\alpha t}) \quad \cdots\cdots (10)^*$$

**Determination of $A$**

The solubility of a gas, $A$, was determined in the first place, from the experimental results and then corrected analytically. The first estimated value of $A$ is obtained from $z$ - $t$ diagram, by extrapolating the curve to the infinite value of $t$. Then, using this value, log $(A-z)$ is plotted against $t$. If Formula (10) is valid, it is sure that the plot of log $(A-z)$ must be rather linear against $t$, in the interval where $t$ is relatively small. However, with the increase of $t$, it is clear, from the nature of logarithm that the curve will show a tendency to bend upwards or downwards, according as the first estimate of $A$ is too great or too small. If the curve is bending downwards, some value is to be added to the first estimate, in order to get

* Formula (10) is quite similar in form, to Formula (1), except that, in the former, $A$ represents a constant, but in the latter, it should be essentially a variable dependent on the time.




Text-fig. 8. Log $(A-z)$ - $t$ diagram for oxygen-methyl oleate

a straight line. Then, we have the second estimate, and so forth, we find finally the appropriate value of $A$, which makes the curve to be straight.

**Determination of $\alpha$**

The value of $\alpha$ was determined by the *method of averages*, using a formula derived from Formula (10),

$$\alpha = 2.303 \frac{n \log A - \Sigma \log (A-z)}{\Sigma t} . \quad \cdots\cdots\cdots\cdots\cdots\cdots (11)$$

In this way, we have different value of $\alpha$, for each different pressure of the same combination of solute and solvent. However, the value of $\alpha$ obtained for a definite solute-solvent system, were found to be much the same, irrespective of pressure applied. The difference appears to be ascribable to the experimental error. At least,

we could not find any orderly relationship between the magnitude of $\alpha$, and the pressure at which the absorption test was carried out. It seems likely that, within such narrow range of pressures, $\alpha$ remains approximately constant, though it is not a theoretical consequence. For that reason, only the mean value of $\alpha$ is given for each system, in Table 3.

**Comparison of Absorption Rate**

Differentiation of Formula (10) gives,

$$\frac{dz}{dt} = \alpha A\, e^{-\alpha t} \quad \cdots\cdots (12)$$

Formula (12) indicates that the absorption rate at a chosen time, $t$, depends upon the magnitude of $\alpha$, $A$, and $e^{-\alpha t}$, of which the first two are constant independent of the time, while the last is decreasing with the time. It follows therefore, that the initial absorption rate is given only by $\alpha A$, but the rate at a later period, is decreasing herefrom, with the increase of $t$, and the decrease in the absorption rate is more and more rapid, the greater the value of $\alpha$. That is to say, an absorbing system which is greater in the initial rate, is not necessarily greater in the later rates. In general, such a system may become rather smaller in the later rates, than a system with smaller initial rate.

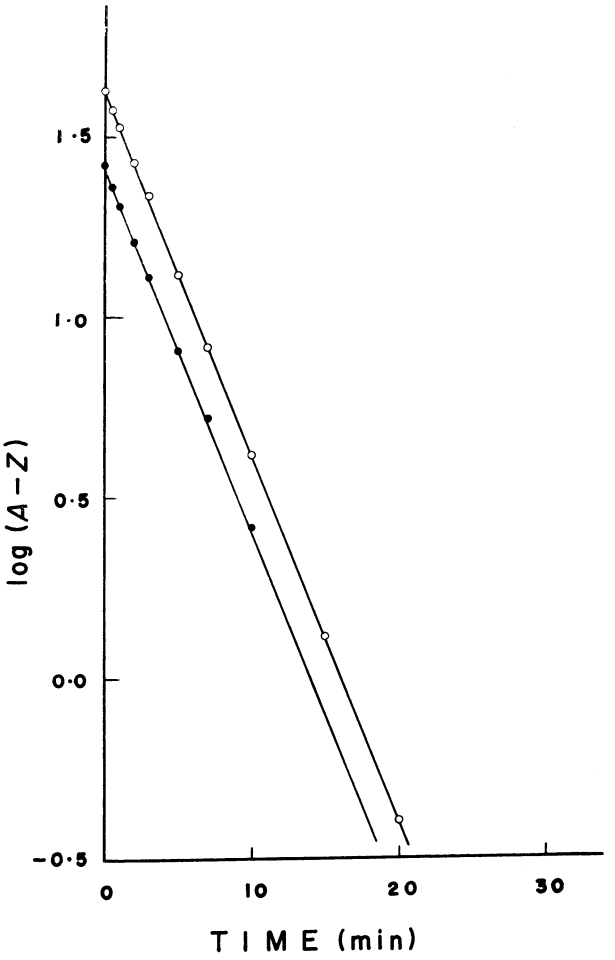
Thus, it might be difficult to decide at what time we are to compare the absorption rates of different systems. However from Formula (10), the time required to reach $1/n$ saturation is given by

$$t_n = \frac{1}{\alpha} \ln \frac{n}{n-1} \quad \cdots\cdots (13)$$

Formula (13) states that the time required to reach a certain proportion of saturation depends, not on the magnitude of $A$, but merely on the value of $\alpha$. The time-length up to real saturation is mathematically infinite in any system, as seen from Formula (13). So that, it can not be the object of comparison. However, the time-length up to a chosen proportion of saturation is finite and inversely proportional to the magnitude of $\alpha$. Therefore, as far as only such time-length is in question, $\alpha$ can be the unique measure to compare the different systems.

However, $\alpha$ represents neither the magnitude of absorption rate at a certain instant, nor the integral amount until a certain time. If $\alpha$ is the same in two systems, the time required to reach a definite proportion of the saturation is the same, no matter what the magnitude of $A$. However, the absorption rate at this time, or the total amount absorbed until this time, is $m$-times as great in the one system as in the other, when the value of $A$ is $m$-times as great in the former system as in the latter.

Therefore, if we want to compare the absolute magnitude of the absorption rate at a certain time, or of the integral amount until a certain time, it is clearly not sufficient to compare merely the magnitude of $\alpha$ in any two systems. For this



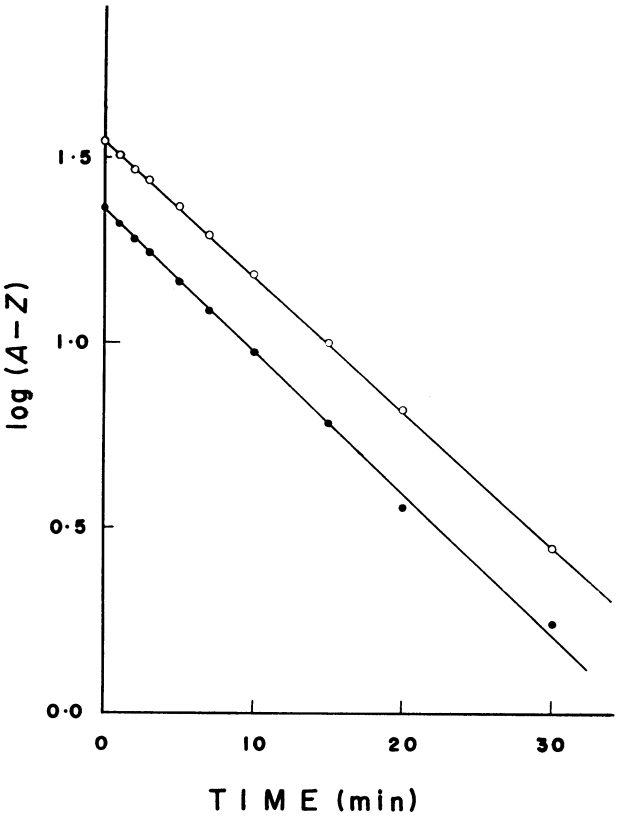

Text-fig. 9. Log $(A-z)$ - $t$ diagram for oxygen-methyl elaidate

reason, the value of $\alpha A$, together with the value of $\alpha$, is given in Table 3. Further discussion will be made later, in this respect (p. 124).

## RESULT

### Solubility

Figure 1, 2 and 3 show the solubility of carbon dioxide, oxygen and nitrogen, respectively, plotted against the pressure as abscissae. The solubility is expressed in terms of volume (cc) of a gas, reduced to standard state, per 100 g of a solvent. Each solubility value was determined from the absorption curve which was traced till the saturation was nearly reached, by extrapolating the curve to the infinite value of time, and by further applying such graphical operation as has been noted (p. 116).



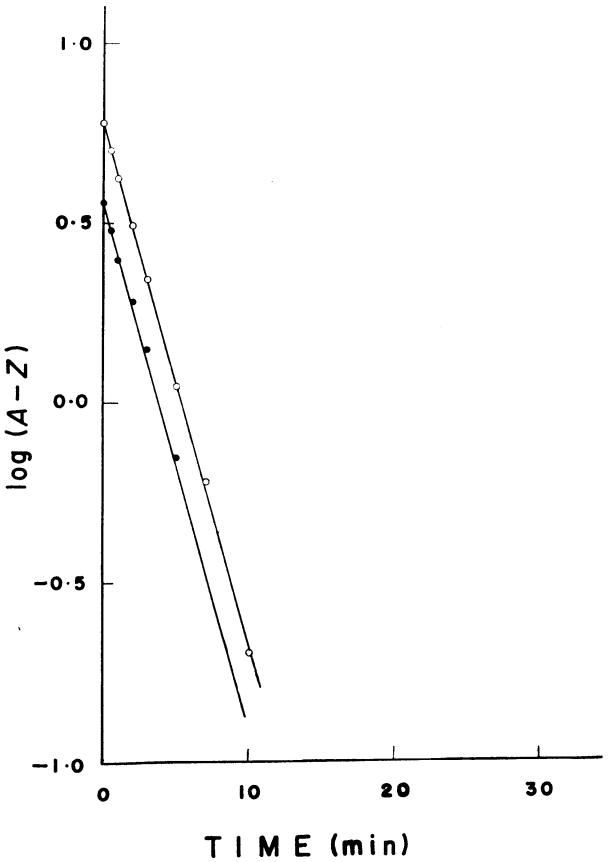

Text-fig. 10. Log $(A-z)$ - $t$ diagram for oxygen-oleic acid.

It is clear, from Figure 1, 2 and 3, that the solubility is a linear function of the pressure, in every solute-solvent system. That is, it obeys Henry-Raoult's law on the diluted solution of a gas. So that, in the present series of experiments, every solubility can be stated by Formula (2).

Table 2 Solubility of gases in materials

| Solute / Solvent | Carbon dioxide | | Oxygen | | Nitrogen | |
|---|---|---|---|---|---|---|
| | $A/p$ cc/100g, atm | ratio | $A/p$ cc/100g, atm | ratio | $A/p$ cc/100g, atm | ratio |
| Methyl oleate | 176. 1 | 3. 0 | 15. 4 | 6. 4 | 10. 1 | 8. 0 |
| Methyl elaidate | 168. 5 | 2. 9 | 16. 6 | 6. 9 | 9. 5 | 7. 5 |
| Oleic acid | 125. 1 | 2. 1 | 14. 4 | 6. 0 | 8. 0 | 6. 3 |
| Water | 58. 8 | 1. 0 | 2. 4 | 1. 0 | 1. 27 | 1. 0 |

In Table 2, is shown the value of $A/p$, which is expressed in terms of the said solubility per atmospheric pressure. Column headed by "ratio" shows the ratio of solubility of each gas in each solvent, to the solubility of the same gas in water.



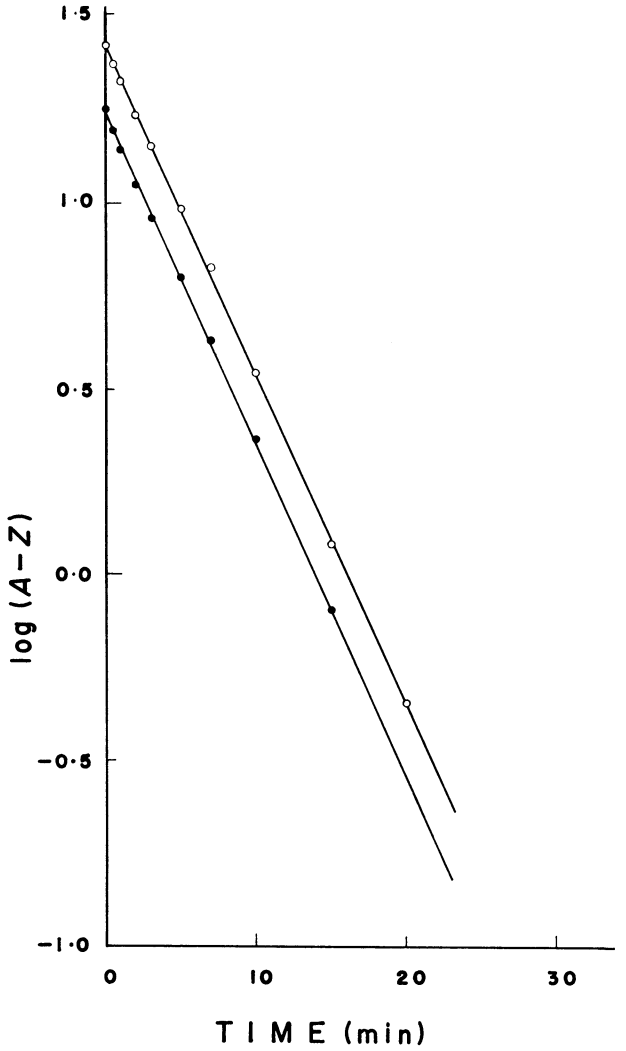

Text-fig. 11. Log $(A-z)$ - $t$ diagram for oxygen-water.

It is seen, from Figure 1 and Table 2, that no remarkable difference exists between the solubility of carbon dioxide in methyl oleate and that in methyl elaidate. In both substances, the solubility of carbon dioxide is about 3 times as great as the solubility of the same gas in water. On the contrary, free oleic acid shows a clearly smaller absorbing capacity of carbon dioxide, than methyl oleate and methyl elaidate.

In the cases of oxygen and nitrogen, the tendency is almost, in accord with the case of carbon dioxide. The solubility of each of the two gases in methyl oleate is not noticeably different from the solubility of the same gas in its *trans*-isomer. Oleic acid shows fairly smaller absorbing capacity of these gases than methyl oleate or -elaidate.

It is also seen from Table 2, that the solubility of nitrogen, as well as that of carbon dioxide, in methyl oleate is greater than in methyl elaidate. Whereas, this order is reversed in the case of oxygen; the solubility is smaller in methyl oleate than in methyl elaidate. However, there is not recognized so great difference, in the solubility of any gas tested, between methyl oleate and methyl elaidate, that this reversion can be regarded as of significance.

In short, it can be stated that methyl oleate and its *trans*-isomer show no great



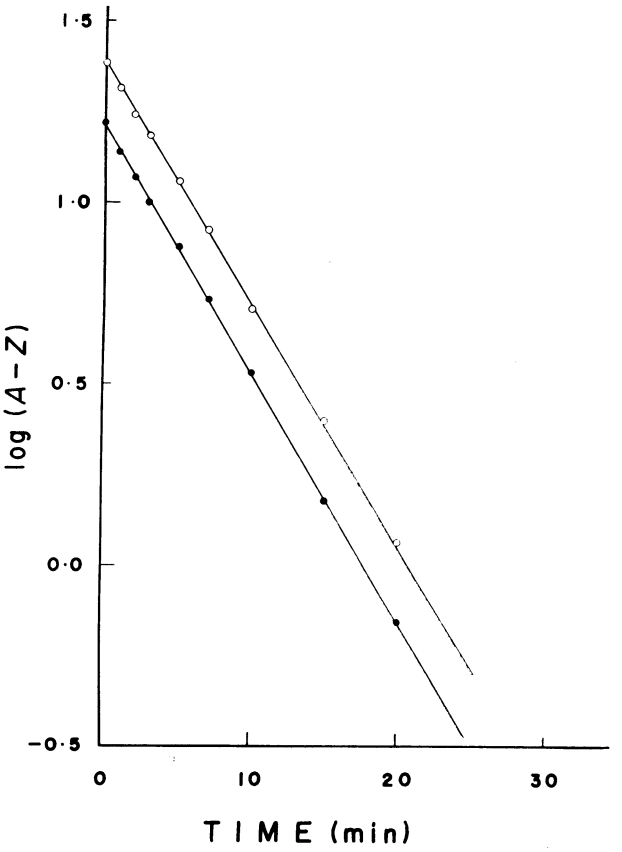

Text-fig. 12. Log $(A-z)$ - $t$ diagram for nitrogen-methyl oleate.

difference in the solubility of any gas tested, while free oleic acid is clearly inferior in this property. Free elaidic acid was not tested, because of its intolerably high melting point.

Finally, in the case of oxygen and nitrogen, "ratio" cited in Table 2, is prominently great, ranging from 6 to 8. While, with carbon dioxide, this value amounts only to 2 or 3. This may be ascibable to the extraordinarily great solubility of carbon dioxide in water.

### Absorption Rate

Figure 4 to 15, each figure gives $\log(A-z)$ - $t$ diagram for each solute-solvent system, each involving two curves represented at two pressures. In each figure, it



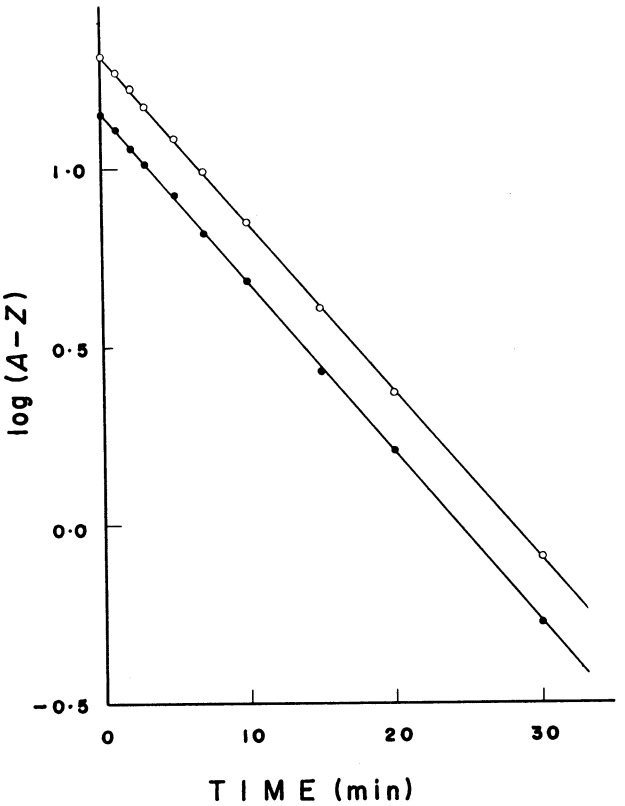

Text-fig. 13. Log $(A-z)$ - $t$ diagram for nitrogen-methyl elaidate.

will be seen that the gradients of two curves involved are nearly similar to each other, irrespective of pressure applied. That is, the value of $\alpha$ appears experimentally constant within this range of pressures. The value of $\alpha$ was determined arithmetically from the points belonging to each curve, by using Formula (11), and the mean value was given for each system, in Table 3.

Table 3 shows the value of $\alpha$ thus obtained, together with the value of $\alpha A/p$. $\alpha$ is a constant characteristic of a solute-solvent system, representing the rapidity to

Table 3 The magnitude of $\alpha$ and $\alpha A/p$

| Solvent \ Solute | Carbon dioxide | | Oxygen | | Nitrogen | |
|---|---|---|---|---|---|---|
| | $\alpha$ min$^{-1}$ | $\alpha A/p$ cc,(100g)$^{-1}$, atm$^{-1}$,min$^{-1}$ | $\alpha$ min$^{-1}$ | $\alpha A/p$ cc,(100g)$^{-1}$, atm$^{-1}$,min$^{-1}$ | $\alpha$ min$^{-1}$ | $\alpha A/p$ cc,(100g)$^{-1}$, atm$^{-1}$,min$^{-1}$ |
| Methyl oleate | 0. 126 | 22. 2 | 0. 197 | 3. 0 | 0. 206 | 2. 1 |
| Methyl elaidate | 0. 107 | 18. 0 | 0. 235 | 3. 9 | 0. 158 | 1. 5 |
| Oleic acid | 0. 068 | 8. 5 | 0. 087 | 1. 9 | 0. 108 | 0. 86 |
| Water | 0. 171 | 10. 1 | 0. 289 | 0. 69 | 0. 186 | 0. 23 |

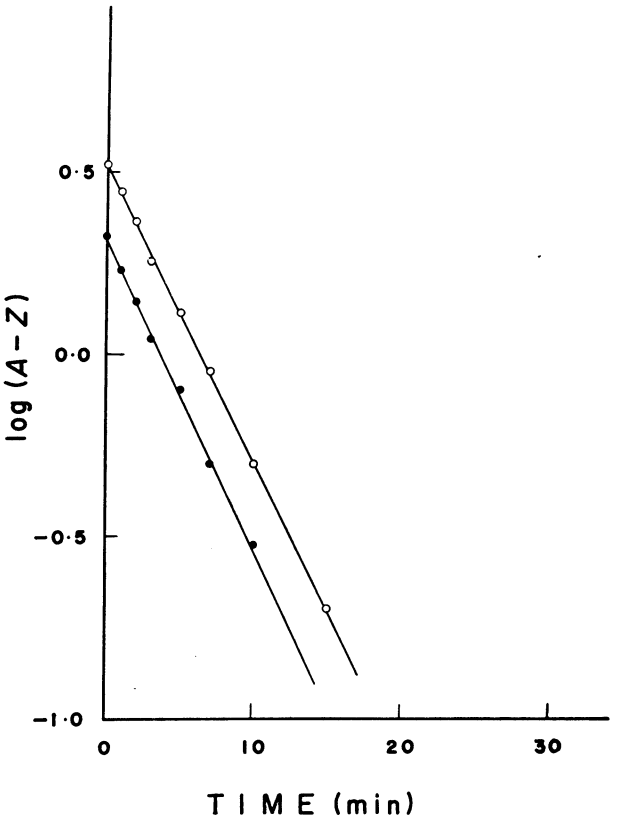



Text-fig. 14. Log $(A-z)$ - $t$ diagram for nitrogen-oleic acid.

approach the saturation. $\alpha A$ represents the initial absorption rate itself, of a system. However, further reference may be made to the next points.

It is certain that the reversion of the absorption rates occurs during the course of the process, between two different systems, as mentioned above (p. 118). However, in two systems (system 1 and 2), (1) if $\alpha_1 > \alpha_2$, $A_1 \geq A_2$, the integral amount, $z$ is always greater in system 1 than in system 2; (2) if $\alpha_1 = \alpha_2$, $A_1 > A_2$, $z$ is at any time, greater in system 1 than in system 2, and in this case, the reversion of the rates can never occur; and (3) if $\alpha_1 < \alpha_2$, $A_1 > A_2$, the two curves have a crossing point, and this point farther, $z$ is greater in system 1 than in system 2. In this sense, we regard $\alpha A$, as the important criterion which measures the absorption rapidity.

Some comparison will be made here. In absorbing carbon dioxide, $\alpha$ is great in the decreasing order of water, methyl oleate, -elaidate and oleic acid. This order is conserved with regard to $\alpha A/p$, except that water falls in its rank from the first to the third. As for the absorption of oxygen, $\alpha$ is great in the order of water, methyl elaidate, -oleate and oleic acid. This order holds for $\alpha A/p$, but water falls from the first to the last. In the case of nitrogen, $\alpha$ is great in the descending order of methyl oleate, water, methyl elaidate and oleic acid. This order is valid for that of $\alpha A/p$, except that water falls from the second to the last.




Text-fig. 15. Log $(A-z)$ - $t$ diagram for nitrogen-water.

Making a long story short, the question resolves itself into the following three points: (1) the magnitude of $\alpha$ is in every case, greater for water than for the esters and the acid tested, whereas, $\alpha A/p$ is smaller for water than for the esters and the acid; (2) among the oily substances examined, esters far excel the free acid in the magnitude of $\alpha$, as well as in the magnitude of $\alpha A/p$; (3) between the two esters, both $\alpha$ and $\alpha A/p$ are greater for methyl oleate, in the case of carbon dioxide and nitrogen, but in the case of oxygen, the order is reversed. With any gas tested, however, neither $\alpha$ nor $\alpha A/p$ differs greatly between methyl oleate and -elaidate.

## CONCLUSION

Concerning *cis*- and *trans*-forms of 9-octadecenoic acids, classical view was rather inclined to the opinion that ordinary oleic acid is *trans*-form and that elaidic acid derived from oleic acid artificially, is *cis*-form. Later, however, MÜLLER and SEARER[10], G. M. ROBINSON and R. ROBINSON[11], KEFFLER[12], and others maintained on the basis of their experimental results, that this theory is wrong and the reverse is the case. At present, this latter opinion appears of great importance.

In the present article, attention was directed to the gas absorbing properties of

methyl oleate and its *trans*-isomer, for the purpose of verifying the hypothesis that the gas absorbing properties might be associated with the length or the shape of the molecule of the solvent. However, the result as a whole, led to the conclusion that these properties does not largely depond on, at least, the *cis-trans* isomerism. We could not find any great difference, either in the solubility of a gas, or in the absorption rate of a gas, between methyl oleate and methyl elaidate.

However, it was found that absorbing capacity and especially absorption rate are smaller in free oleic acid than in methyl oleate and -elaidate. It is seen from Table 3, that for any gas tested, the magnitude of $\alpha$ and $\alpha A/p$, is only about a half as great in oleic acid as in methyl oleate or -elaidate.

It is also seen, as far as the present article is concerned, that the decreasing order of viscosity is consistent with the increasing order of the magnitude of $\alpha$ (compare Table 1 and 3). However, it seems to the author that this cannot be a general rule, because, as was reported[1], the viscosity of oleic acid is very adjacent to that of sperm head oil at 35°, despite that the former absorbs gases far far slowly than the latter.

## SUMMARY

Gas absorbing properties of methyl oleate and methyl elaidate were studied in comparison, in order to ascertain the experimental hypothesis that these properties might be associated with the *cis-trans* isomerism.

The result, however, led to the conclusion that no great difference exists between methyl oleate and its *trans* isomer, not only in the absorption rate but also in the absorbing capacity of the gases tested.

Free oleic acid was also investigated, with the restlt that it is smaller in the absorbing capacity and far smaller in the absorption rate, than methyl oleate or methyl elaidate.

In the present article, the author used a formula which was obtained for combining the first-order reaction formula and Henry-Raoult's law for diluted solution of a gas, with the result that the formula obtained is valid for the relation between the absorbed amount of the gases and the time, within the limits of experimental error.

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## Methyl oleate 及びその立体異性体のガス吸収能について

石　川　安　太　郎

前報[1)·2)·3)]で報告したように，油状物質 (Glycerides, Sperm waxes, 其他) は水に比して極めて大きいガス吸収能を持っているが，特に Sperm wax のような長鎖状ワックスはそのガス吸収容（即ち溶解度）において優れているのみならず，特にガス吸収速度において他の油状物質を大きく引離している．

以上のことから Sperm wax のような長鎖状物質はガス吸収容，特に吸収速度において優れているだろうことが推察される．

本報においては，溶媒の分子の長さがガス吸収容及び吸収速度と関係があるのではないかという想定の下に，Methyl oleate 及びその *Trans*-isomer である Methyl elaidate の $CO_2$, $O_2$ 及び $N_2$ の吸収能について調べられた．又比較の為に遊離 Oleic acid 及び水についても，全く同様の実験を行った．

本報における第一の焦点は従って，この二つの *Cis-trans* 異性体がガス吸収上どのような相違を示すかということであり，第二の焦点は Oleic acid とその Methyl-derivative との比較である．気体一液体系の溶解の機作が明かにされてはいないように思われるので，その意味で，この実験から何等かの示唆が得られることを期待した次第である．

気体一液体系の溶解において溶解の速度は，大体において一次反応式で表わされることが，前報[2) 3)]から明かであるが，それは $N_2$, $O_2$ の場合のように溶解度が小さい時に限られ，$CO_2$ のように溶解度の大きいものではこの式を適用することが無理である．著者は一次反応式と Henry-Raoult の法則を組合せて，何れの場合にもよくあてはまる実験式を誘導し，これを用いた．

実験の結果の大要は次のようである．

1) Methyl oleate とその *trans* 異性体は $CO_2$, $O_2$ 及び $N_2$ の吸収において，吸収容においても吸収速度においても，大きな差を示さない．

2) 遊離 Oleic acid はこの両者に比較してガス吸収容において劣り，特に吸収速度において遙かに劣る．

3) 本報の結果に関する限り，溶媒の粘度と吸収速度の間には何か規則的関係があるように見えるが，これは前報の実験結果から見て一般的な rule とはなり得ない．

結論として溶媒の分子の長さとガス吸収能の間に関係があるだろうという実験的仮設が全面的に

否定されたとはいえないが，Methyl oleate とその *trans* 異性体の間にはガス吸収能において，大きな相異がないことが判明した．しかし遊離 Oleic acid とその Methyl-derivative の間にはガス吸収容においても相当な差があり，特に吸収速度においては前者は後者の約半分であるということは何等かの興味があることのように思われる．